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## (54) PROCESS FOR PREPARING BUTANEDIOL-(1.4)

(71) We, HOECHST AKTIEN - GESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a single-stage, catalytic process for preparing butanediol-(1.4) from maleic anhydride, maleic acid or mixtures thereof.

Butanediol-(1.4) is used, for example, as a starting material for preparing polyester fibers; in this process butanediol-(1.4) is reacted, for example, with terephthalic acid at an elevated temperature in the presence of catalysts to yield polybutylene terephthalate.

Processes for preparing butanediol-(1.4) are already known. In addition to a number of processes based, for example, on acetyleneformaldehyde or 1.4-dihalobutane, processes for preparing butanediol-(1.4) from  $\gamma$ -butyrolactone have recently been described.

Economic and technically useful processes for preparing butanediol-(1.4) directly from maleic anhydride or maleic acid have not been proposed hitherto. It is true that maleic anhydride may be converted into butanediol-(1.4) in a yield of at most 64%, but the Raney cobalt used as catalyst in this process is unsuitable for continuous operation, since it is dissolved and irreversibly deactivated by maleic anhydride and by maleic acid formed as an intermediate even after a short period. The reaction also re-

quires extremely high pressures of about 800 bars and temperatures of about 275°C, at which the diol formed is dehydrated with considerable formation of tetrahydrofuran.

When using nickel molybdate or nickel chromate catalysts described in known processes, butanediol-(1.4) is obtained from maleic anhydride in a yield of about 50% only besides considerable quantities of tetrahydrofuran. This process also requires very high pressures of about 800 bars which may only be obtained with difficulty. The catalysts are also unstable in prolonged use and are dissolved and deactivated by acids, like the copper chromium oxides known for ester hydrogenation. The same applies to pure nickel catalysts.

When using catalysts which are described as being more stable towards acids and contain for example rhenium, rhenium-molybdenum-cobalt, nickel-molybdenum-rhenium or nickel-rhenium, maleic anhydride or maleic acid can be converted into butanediol-(1.4) up to at most 9 to 14%. In this process there are formed as main products generally in a yield of more than 90% succinic acid, tetrahydrofuran and  $\gamma$ -butyrolactone. In this case also, dissolution, especially of the nickel or cobalt portions of the catalysts, takes place. In other cases no butanediol-(1.4) is formed from maleic anhydride or maleic acid when using rhenium catalysts, but only succinic acid. The same applies to platinum and rhodium catalysts. When using palladium catalysts, for example palladium/carbon catalysts, takes place. In other cases no butanediol-(1.4) is formed from maleic anhydride or maleic acid when using rhenium catalysts, but only succinic acid. The same applies to

- platinum and rhodium catalysts. When using palladium catalysts, for example palladium/carbon catalysts, maleic anhydride may be hydrogenated only to the stage of  $\gamma$ -butyrol-actone or the reaction is stopped at the succinic acid stage.
- The present invention is based on the observation that maleic anhydride or maleic acid or mixtures thereof may be converted directly into butanediol-(1.4) in a one-step catalytic reaction with excellent yields and conversions and a very high service life of the catalysts.
- This is very surprising since acceptable yields have been obtained hitherto only with unstable catalysts completely unsuitable for prolonged technical use. When more stable catalysts are used very low yields of butanediol-(1.4), if any, or succinic acid only, are obtained.
- The present invention provides a process for preparing butanediol-(1.4) which comprises hydrogenating maleic anhydride, maleic acid or a mixture thereof in the presence of a catalyst comprising an element of group VIIA of the Mendeleef Periodic Table or a compound thereof and ruthenium, rhodium, palladium, osmium, iridium, or platinum or a mixture of such elements and compounds.
- The process of the present invention is especially distinguished by the fact that practically no by-products such as tetrahydrofuran,  $\gamma$ -butyrolactone and succinic acid are obtained and that the formation of n-butanol, disclosed in the literature during hydrogenation of maleic anhydride and maleic acid to tetrahydrofuran and  $\gamma$ -butyrolactone, is insignificant.
- The process of the present invention for preparing butanediol-(1.4) is a technically simple and very economical method, in which problems associated with waste products, which may be observed in the former processes for preparing butanediol-(1.4) from dihalobutanes, do not occur.
- The catalysts used in the process of the present invention contain elements or compounds of elements of group VIIA of the Mendeleef Periodic Table (manganese, technetium and rhenium), and ruthenium, rhodium, palladium, osmium, iridium or platinum or compounds thereof, including mixtures of elements of one group with compounds of elements of the other group. Preferred group VIIA elements are manganese and rhenium. The preferred specified group VIII elements are palladium and platinum. The most preferred catalyst materials are those comprising palladium/rhenium, platinum/rhenium and platinum/palladium/rhenium.
- An especially surprising advantage in the present process resides in the fact that catalyst selectivity may be obtained by simple combination of elements of group VIIA or compounds thereof with the specified group VIII elements or compounds thereof, which cannot be obtained when using elements of one group or compounds thereof alone, especially with rhenium or palladium.
- In addition, it was not to be expected that practically quantitative conversion of maleic anhydride and/or maleic acid could thus be obtained without notably less activity of the catalysts used according to the present invention.
- The combination of the elements of group VIIA with the specified group VIII elements, especially rhenium and palladium, and/or their compounds, has therefore, a surprising, and considerable stabilizing effect and increases significantly the life of the catalysts as compared to those described in the literature. This is of decisive importance for prolonged technical operation and as a result the present process is superior to the prior art processes.
- In the process according to the present invention, the catalysts are generally used in a pulverulent form. They may also be used, however, in a tabletted form or mixed with inert materials which optionally serve as carriers.
- Suitable carriers are, for example: silicon dioxide, titanium dioxide, silicon dioxide-aluminium oxide, carbon, thorium oxide, zirconium oxide, silicon carbide, spinels and aluminium oxide. The carrier may be pulverulent or shaped, for example as granules, pellets, tablets, compressed extruded materials, saddles, rings or tubes having a honeycomb structure.
- If supported catalysts or catalysts mixed with inert materials are used, the quantity of the catalytically active substance is generally in the range from 0.1 to 50% by weight of the total quantity of the catalyst. The quantity of the inert material (carrier) is consequently from 99.9 to 50% of the total weight of the catalyst.
- The weight ratio of the elements of group VIIA to those of group VIII is preferably in the range from 99:1 to 1:99, more preferably from 10:1 to 1:10.
- The catalysts may be present in the form of elements or as compounds or as mixtures of both, optionally together with carriers. Consequently they may be prepared using directly suitable compounds being optionally supported or by reducing these compounds to a greater or lesser extent, optionally to the elements.
- Suitable compounds are, for example: oxides, hydrated oxides, carbonates, nitrates, borides, carboxylates (such as acetates, propionates and butyrates) and chelates of 1, 3-diketo compounds (for example enolates such as acetyl acetonates, benzoyl ace-

tonates and acetoacetic acid ester compounds). Especially suitable are carboxylates, acetylacetonates, oxides and hydrated oxides. For technical and economic reasons, the use of rhenium, for example, in the form of potassium perrhenate or rhenium heptoxide, and of palladium in the form of palladium (II) acetate or acetyl-acetonate is especially advantageous, as these compounds are commercially available.

For preparing, for example, palladium-rhenium catalysts, a solution of a palladium carboxylate or of a compound reacting with a carboxylic acid to yield palladium carboxylate, such as hydrous palladium oxide, palladium nitrate, palladium hydroxycarbonate or a salt of a 1,3-diketo-compound such as acetoacetic acid ester or acetylacetone, in an anhydrous or water-containing carboxylic acid together with perrhenic acid or its salts, is applied to the carrier, for example by impregnating, immersing or suspending the carrier material or by spraying. The carboxylic acid is then eliminated by drying, preferably at an elevated temperature, *in vacuo* or under atmospheric pressure. The catalyst can then be used directly, but is preferably treated with a gaseous or liquid reducing agent at a temperature from 15 to 200°C.

Suitable carboxylic acids are all liquid aliphatic carboxylic acids having of from 2 to 10 carbon atoms which may be vaporized *in vacuo* without being decomposed. Acetic acid, propionic acid and butyric acid are preferably used; especially preferred is acetic acid.

The solutions of both compounds used for preparing the catalysts, for example a palladium salt and a rhenium compound, may be applied separately to the carrier material, but the palladium and rhenium compounds are preferably dissolved in a single carboxylic acid. It is also possible to apply firstly from carboxylic acid solution one of the palladium compounds to the carrier material and to apply subsequently the solution of a rhenium compound in a carboxylic acid.

The reduction of the catalysts may be performed in the liquid phase, for example with hydrazine hydrate, but is advantageously carried out at an elevated temperature, for example from 100 to 200°C, in the gaseous phase with reducing vapours or gases such as hydrogen, methanol, formaldehyde, ethylene, propylene and butene, in a diluted or undiluted form. Strongly diluting at the beginning with inert gases such as nitrogen, carbon dioxide and noble gases and increasing the concentration of the reducing agent as the reduction progresses have proved especially advantageous, so that the reduction may be terminated for example in pure hydrogen. The reduction may be performed in a separate device or in the apparatus used for

converting maleic anhydride and/or maleic acid into butanediol-(1.4).

The catalysts may be pyrophoric. In this case they must be appropriately treated. Reducing the catalyst and reacting maleic acid and/or the anhydride in the same apparatus is especially advantageous in this case.

An important factor in carrying out the single-step direct process of the present invention on an industrial scale is that practically no succinic acid is formed, an acid which would readily precipitate owing to its extremely low solubility and cause obstruction of the apparatus or require a further reaction step.

For carrying out the process of the present invention in an optimum manner, the hydrogenolysis of maleic anhydride and/or maleic acid is generally performed under an elevated pressure and at an elevated temperature.

The reaction temperatures are therefore generally from 50 to 300°C, preferably from 150 to 250°C.

The reaction pressure is generally from 50 to 500 bars, preferably from 100 to 350 bars.

The hydrogen for the hydrogenolysis of maleic anhydride or maleic acid is generally used in a considerable stoichiometric excess. Unreacted hydrogen may be recycled to the reaction zone. The reaction may be carried out continuously or discontinuously. Hydrogen is generally used in a technically pure form. Admixtures of inert gases such as nitrogen, however, do not disturb the course of the reaction.

The reaction time in the process of the present invention is generally from 5 minutes to 8 hours, for example about 3 to 6 hours, when working discontinuously in an autoclave.

Pulverulent catalysts may be filtered off at the end of the reaction or be separated by centrifugation and be reused without a noticeable loss of activity.

When working continuously, for example in the trickling phase, tabletted catalysts or those applied on carriers are generally used.

The solvents generally used in hydrogenations may be used, for example dioxan, tetrahydropyran or other cyclic or straight chain ethers, for example tetrahydrofuran or diethyl ether. Polyalkylene glycol dialkyl ethers, for example tetramethyleneglycol dibutyl ether, tetramethylene-glycol dipentyl ether, tetraethyleneglycol dimethyl ether, tetraethyleneglycol diethyl ether and diethyleneglycol dibutyl ether or mixtures of these or other solvents may also be used. Solvents having a boiling point above 245°C have proved especially advantageous. The content of maleic acid and/or anhydride in the initial solution in this case is generally from 5 to 60% by weight. Using maleic anhydride as a 20 to 40% by weight solution

in 1, 4-dioxan has proved advantageous. Water is also suitable as a solvent for maleic acid. The quantity of catalyst used for the hydrogenation is generally from 0.5 to 25% by weight of the quantity of maleic anhydride or maleic acid.

Maleic anhydride, maleic acid and any mixture of both substances may be used as the starting material.

The reaction mixtures are generally worked up by fractional distillation.

The following method has proved especially advantageous for preparing butanediol-(1.4) discontinuously: to a solution of maleic anhydride in 1,4-dioxan in a high pressure autoclave together with the catalyst, hydrogen is introduced under pressure and the reaction mixture is heated. At the end of the reaction the reaction mixture is cooled, the catalyst is separated and the mixture is distilled by fractionation.

The following Examples illustrate the invention.

#### Example 1:

27g of palladium acetate and 4 g of rhenium heptoxide were dissolved in 1200 ml of acetic acid at 80°C and 100 g of kieselguhr were added. The mixture was evaporated to dryness *in vacuo* while stirring and then reduced in a hydrogen atmosphere at 200°C.

0.5 mol of maleic anhydride (49g) were dissolved in 100 ml of dioxan. The solution was poured into a 1 liter autoclave provided with a shaking device together with 5 g of the pulverulent kieselguhr catalyst containing 10.6% of palladium and 2.3% of rhenium. Hydrogen was introduced until a pressure of 215 bars was reached and the mixture obtained was rapidly heated to 225 to 230°C. After about 6 hours the reaction was interrupted and the reaction mixture was rapidly dried. After separation of the catalyst 151.5 g of a water-clear, colorless reaction solution was obtained containing 27.9 % of 1,4-butane-diol (42.2 g) corresponding to 93.8% of the theory. Besides butanediol-(1.4) and the solvent dioxane, water could be detected as well as rather small quantities of  $\gamma$ -butyrolactone, tetrahydrofuran, n-butanol by gas chromatography and traces of succinic acid by titrimetry.

#### Example 2:

49 g of maleic anhydride were dissolved in 100 ml of dioxane. The solution was reacted together with 5.9 g of the slightly wet catalyst, which had already been used in Example 1 and had been filtered off, in the manner described in Example 1. There were obtained 149.8 of a water-clear colorless solution containing 28.2% of 1,4-butane-diol (42.3 g). This corresponded to 93.9% of the theory. The reaction mixture

contained still small quantities of a polyester besides the substances cited in Example 1.

#### Example 3:

The calculated quantity of platinum acetate and rhenium heptoxide in acetic acid solution was admixed with kieselguhr, dried and reduced as described in Example 1.

A solution of 58 g of maleic acid (0.5 mol) in 200 ml of water was poured into a 1 liter steel autoclave together with 6 g of the kieselguhr catalyst containing 10% of platinum and 2.8% of rhenium. Hydrogen was introduced until a pressure of 195 bars was obtained and the reaction mixture was rapidly heated to 230°C.

After a reaction time of about 3 and a half hours another 25 bars of hydrogen were introduced. After a total reaction time of 5 hours the reaction was stopped, as no further hydrogen absorption could be observed. The catalyst was separated by a centrifuge and 253 g of a reaction solution were obtained.

The water-clear, colorless solution contained 16% or 40.8 g of butanediol-(1.4) corresponding to 90.0% of the theory.

The reaction mixture contained besides butanediol-(1.4) and water 0.53% of  $\gamma$ -butyrolactone, 0.6% of n-butaneol as well as small portions of tetrahydrofuran, succinic acid and butyric acid.

#### Example 4:

For preparing the desired quantity of the catalyst, palladium acetate, rhodium acetate and rhenium heptoxide were dissolved in the calculated quantities in acetic acid, aluminosilicate powder was added and the mixture was dried and reduced as described in Example 1. Then 0.5 mol of maleic anhydride (49 g) were dissolved in 100 g of tetrahydropyran (about 114 ml). 5.2 g of the kieselguhr-aluminium oxide catalyst were added containing 8.3% of palladium, 4.2% of rhodium and 2.7% of rhenium and the mixture was placed into a 0.5 liter autoclave provided with a magnetic type lifting stirrer. After having introduced hydrogen until a pressure of 189 bars was obtained the mixture was rapidly heated to 220°C and allowed to reaction for a total of 4 and a half hours. Thereafter it was rapidly cooled, the catalyst was separated and the reaction mixture was analyzed by gas chromatography.

147g of a solution were obtained containing 26.9% of butanediol-(1.4) (39.6 g), which corresponded to about 88% of the theory.

#### Example 5:

For preparing the catalyst 100 g of active carbon (810 m<sup>2</sup>/g according to BET, pore volume of 0.9 ml/g) were impregnated with a solution of 20 g of Na<sub>2</sub>PdCl<sub>4</sub> in 86 ml of water, dried while stirring, impregnated

with a solution of 4 g of NaOH in 88 ml of H<sub>2</sub>O and allowed to stand for 2 hours. Thereafter the mixture was washed until it was free from chloride, dried to a weight of 150 g, impregnated with a solution of 6 g of Re<sub>2</sub>O<sub>7</sub> in 50 ml of water, dried while stirring and reduced in hydrogen at 200°C.

0.25 mol of maleic anhydride (24 g) and 0.25 mol of maleic acid (29 g) were dissolved in 100 ml of slightly heated dioxan 5 g of the catalyst based on active carbon powder were added which contained 4.1% of rhenium and 8.2% of palladium oxide and the mixture was poured into a 0.5 liter high pressure autoclave provided with a shaking device.

After having introduced hydrogen until a pressure of 170 bars was obtained, the mixture was heated to 232°C and allowed to react for 3 hours. Another 40 bars of hydrogen were introduced and the reaction mixture was rapidly cooled after 1.5 hours. The catalyst was then separated from the mixture.

149.3 g of reaction solution were obtained containing 39.8 g of butanediol-(1.4).

#### Example 6:

The kieselguhr catalyst used in Example 1 was compressed to tablets having a diameter of 6 mm and a thickness of 2 mm on a pelleting machine. 1 liter of this catalyst was poured into a stainless steel high pressure reactor having a length of about 2 m. The apparatus was flushed with nitrogen and hydrogen was slowly added until a pressure of 260 bars was attained. While adding hydrogen at the lower end of the reactor a 32% solution of maleic anhydride in dioxan was added at the upper end and allowed to trickle over the catalyst. As soon as a liquid left the reactor at the lower end, the reaction mixture was slowly heated to the working temperature of 225°C while continuing the addition of hydrogen at a rate of about 8 to 10 Nm<sup>3</sup>/h (N meaning that the volume is calculated under normal conditions of temperature and pressure i.e. of 0°C and 760 mmHg) and dioxan-maleic anhydride at a rate of about 1520 g/h. Two hours after having attained the working temperature of 225°C the leaving reaction mixture was analyzed at hourly intervals. Per hour there were obtained about 1560 g of reaction mixture containing on the average from 25 to 26% of butanediol-(1.4), which correspond to about 85 to 90% of the theoretical yield of butanediol-(1.4). A decrease of the output could not be observed even after 300 working hours.

#### Example 7:

20 g of palladium acetate, 10 g of iridium acetate and 4 g of rhenium heptoxide were dissolved in 600 ml of glacial acetic acid and

100 g of kieselguhr were introduced by stirring; the mixture was dried in a rotary evaporator at 60°C in a water jet vacuum. The dried catalyst was reduced in an aqueous solution of a sodium borohydride at a temperature of 40°C, then washed and dried. It contained 8.2% of palladium, 4% of iridium and 2.3% of rhenium as borides, the percentages being calculated on the elements.

5 g of this catalyst were placed in an autoclave with 0.5 mol of maleic anhydride and 100 ml of dioxan and treated as described in Example 1.

148.1 g of a water-clear colorless reaction solution were obtained containing 39.8 g of butanediol-(1.4).

#### Example 8:

19.5 g of palladium acetate, 7.7 g of ruthenium acetate and 3.3 g of rhenium heptoxide were dissolved in 900 ml of acetic acid, 100 g of zirconium oxide were introduced by stirring, the mixture was dried in a rotary evaporator *in vacuo* and reduced in hydrogen at 200°C.

0.5 mol of maleic acid (58 g) were dissolved in 100 ml of warm dioxan. 7.5 g of a zirconium oxide catalyst containing 8.1 % of palladium, 2.5% of ruthenium and 2.2 % of rhenium were added and the mixture was placed into a 0.5 liter autoclave provided with a magnetic type lifting stirrer. Hydrogen was introduced until a pressure of 178 bars was obtained, the mixture was rapidly heated to 215°C and allowed to reaction for 3 and a half hours. The mixture was cooled, the pressure released and the reaction solution was analyzed. After having filtered off the catalyst 138 g of a solution containing 24.8% or 34.9 g of butanediol-(1.4) was obtained, which corresponded to about 78 % of the theory.

#### Comparative Example 1:

27 g of palladium acetate were dissolved in 1200 g of glacial acetic acid at 80°C and 100 g of kieselguhr were added. This mixture was dried and reduced as described in Example 1.

0.5 mol of maleic acid (149 g) were dissolved in 100 ml of dioxan. The solution was reacted in the manner described in Example 1 with 5 g of the kieselguhr catalyst containing 10 % of palladium.

148.3 g of a slightly yellow solution were obtained, containing only 3.5 % (5.2 g) of butanediol-(1.4). The main product of the reaction was  $\delta$ -butyrolactone being present in the reaction solution in an amount of 23.1 %.

#### Comparative Example 2:

3.2 g of rhenium heptoxide were dissolved in 400 ml of glacial acetic acid and 100 g of kieselguhr were introduced by stirring this mixture was dried and reduced as described

in Example 1.

The hydrogenation was carried out as described in Comparative Example 1, but by using instead of the catalyst used therein 5 g of the SiO<sub>2</sub> catalyst containing 2.3 % of rhenium. 147.2 g of a reaction solution were obtained containing only traces (<0.2 %) of butanediol-(1.4), 10.2 % of  $\gamma$ -butyrolactone but more considerable quantities of succinic acid, partly precipitating.

WHAT WE CLAIM IS:-

1. A process for preparing butanediol-(1.4) which comprises hydrogenating maleic anhydride, maleic acid or a mixture thereof in the presence of a catalyst comprising an element of group VIIIA of the Mendeleef Periodic Table or a compound thereof and ruthenium, rhodium, palladium, osmium, iridium or platinum or a compound thereof or a mixture of such elements and compounds.

2. A process as claimed in claim 1, wherein the group VIIA element is manganese or rhenium.

3. A process as claimed in claim 1, wherein the catalyst comprises rhenium or a compound thereof and palladium and platinum or a compound thereof.

4. A process as claimed in claim 1, wherein the catalyst comprises rhenium or a compound thereof and palladium or a compound thereof.

5. A process as claimed in any one of claims 1 to 4, wherein the compounds are oxides, hydrated oxides, carboxylates, chelates of 1,3-diketo compounds, nitrates, carbonates or borides.

6. A process as claimed in any one of claims 1 to 5, wherein the catalyst is supported on a carrier material.

7. A process as claimed in claim 6, wherein the quantity of catalytically active substance is from 0.1 to 50% by weight of the total quantity of the catalyst.

8. A process as claimed in claim 6 or

claim 7, wherein the carrier material is silicon dioxide, silicon dioxide/aluminium oxide, carbon, titanium dioxide, thorium oxide, zirconium oxide, silicon carbide, a spinel or aluminium oxide.

9. A process as claimed in any one of claims 1 to 8, wherein the weight ratio of the element of group VIIA to ruthenium, rhodium, palladium, osmium, iridium or platinum is from 99:1 to 1:99.

10. A process as claimed in any one of claims 1 to 9, wherein the reaction temperature is from 50 to 300°C.

11. A process as claimed in any one of claims 1 to 10, wherein the reaction pressure is from 50 to 500 bars.

12. A process as claimed in claim 4, wherein the catalyst is prepared by applying a carboxylic acid solution of a palladium carboxylate or of a palladium compound yielding a carboxylate in the presence of a carboxylic acid, together with perrhenic acid or a salt thereof, to a carrier material, removing the carboxylic acid by drying *in vacuo* or under atmospheric pressure and treating the catalyst with a gaseous or liquid reducing agent at a temperature of from 15 to 200°C.

13. A process as claimed in claim 12, wherein the liquid aliphatic carboxylic acid has from 2 to 10 carbon atoms, and is vaporizable *in vacuo* without being decomposed.

14. A process as claimed in claim 1 carried out substantially as described in any one of Example 1 to 8 herein.

15. A process as claimed in claim 12 carried out substantially as described in any one of Example 1, 4, 7 and 8 herein.

16. Butanediol-(1.4) whenever prepared by a process as claimed in any one of claims 1 to 15.

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